Europäisches Patentamt

European Patent Office

Office européen des brevets

(11) Publication number: **0 015 132**
A1

EUROPEAN PATENT APPLICATION

Application number: 80300463.9

Date of filing: 19.02.80

(51) Int. Cl.³: **C 01 B 33/28**
B 01 J 29/28

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(54) Crystalline zeolitic material, synthesis and use thereof.

(57) A new crystalline zeolitic material, designated ZSM-48, the composition of which expressed in terms of moles per 100 moles of silica, usually falls within the range:
(0 to 15)RN : (0 to 1.5)$M_{2/n}O$: (0-2)Al_2O_3 : (100)SiO_2 wherein M is at least one cation having a valence n, RN is a C_1-C20 organic compound, having at least one amine functional group of $pK_a \geq 7$. ZSM-48 is characterized by the distinctive X-ray powder diffraction pattern shown in Table I, and is prepared from a reaction mixture comprising a source of silica, C_1-C_{18} organic compounds as defined above, with or without a source of alumina, and water.
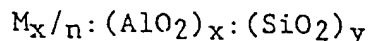
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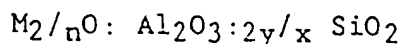# CRYSTALLINE ZEOLITIC MATERIAL, SYNTHESIS AND USE THEREOF

This invention relates to a new crystalline zeolitic material, to a method for synthesising it, and to its use, inter alia as organic conversion catalyst.

Many crystalline zeolites are known, in most cases as aluminosilicates. Some occur (at least so far) only in nature, for instance paulingite and merlinoite; some occur only as a result of synthesis, for instance zeolites A and ZSM-5; and some occur in both natural and synthetic forms, for instance mordenite, a synthetic counterpart of which is known as Zeolon, and faujasite, synthetic counterparts of which are known as zeolites X and Y. Counterparts are of course demonstrated as such by correspondence of their X-ray diffraction data, the indicia by means of which the individuality of a zolite is established. Such data are a manifestation of the particular geometry of the three-dimensional lattice, formed of SiO_4 and in most cases AlO_4 tetrahedra crosslinked by the sharing of oxygen atoms and including sufficient cationic complement to balance the resulting negative charge on any AlO_4 tetrahedra, of which a zeolite may consist.

The chemical formula of an aluminosilicate zeolite is thus

$$M_{x/n}:(AlO_2)_x:(SiO_2)_y$$

where M is a cation of valence n and x and y are the number of aluminum and silicon atoms, respectively, in the unit cell (the geometric unit which repeats throughout the extent of the lattice). This expression is however frequently transmuted into the "mole ratio of oxides" form,

$$M_{2/n}O: Al_2O_3:2y/x \ SiO_2$$

which is of course empirically ascertainable and thus the only formula which can be ascribed to a zeolite when

its unit cell contents are unknown. Since the only significant quantity in such a formula is the term $2y/x$, and since this term (which is almost invariably a range) can usually be satisfied by many zeolites of widely differing lattice geometry, chemical formula is not uniquely restrictive in establishing the identity of a zeolite. Furthermore, such a formula frequently expresses artefact when empirically derived, the cationic-valence/aluminum-atoms ratio deviating from unity, and it fails to provide for zeolites whose lattice structure can be brought into existence from reaction mixtures from which alumina is excluded. Moreover, both the unit cell formula and the "mole ratio of oxides" formula imply that the geometrical identity which persists between succeeding unit cells is accompanied by their compositional identity.

We have now discovered a zeolite having a lattice structure previously unknown, as evidenced by its X-ray diffraction data, which we call ZSM-48.
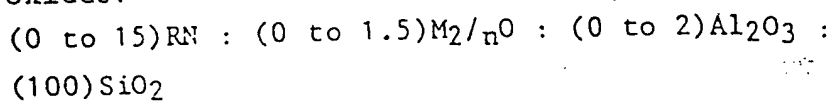
According to the present invention a crystalline zeolitic material, ZSM-48, has a lattice constituted by SiO_4 and possibly AlO_4 tetrahedra crosslinked by the sharing of oxygen atoms and characterized by the following interplanar spacings:

TABLE 1

d(A°)	Relative Intensity
11.8 ± 0.2	W-VS
10.2 ± 0.2	W-M
7.2 ± 0.15	W
4.2 ± 0.08	VS
3.9 ± 0.08	VS
3.6 ± 0.06	W
3.1 ± 0.05	W
2.85 ± 0.05	W

These values were determined by standard
techniques. The radiation was the K-alpha doublet of
copper, and a scintillation counter spectrometer with a
strip chart pen recorder was used. The peak heights, I,
and the positions as a function of 2 times theta, where
theta is the Bragg angle, were read from the
spectrometer chart. From these, the relative
intensities, 100 I/I_0, where I_0 is the intensity of the
strongest line or peak, and d (obs.), the interplanar
spacing in A, corresponding to the recorded lines were
calculated. In Table 1 the relative intensities are
given in terms of the symbols W= weak, VS = very strong,
W-VS and W-M = weak to very strong and weak to medium
respectively. The pattern is preserved upon ion
exchanges, possibly with some minor shifts in
interplanar spacing and variation in relative intensity.
Other minor variations can occur depending on the
silicon to aluminum ratio of the particular sample and
its thermal history.

In the as-synthesised form ZSM-48 usually
manifests the formula in terms of mole ratios of
oxides:

(0 to 15)RN : (0 to 1.5)$M_{2/n}O$: (0 to 2)Al_2O_3 :
(100)SiO_2

wherein M is at least one cation having a valence n and
RN is a C_1-C_{20} organic compound having at least one

amine functional group of $pK_a \geq 7$. The material of course also manifests the distinctive X-ray diffraction pattern shown in Table 1 above.

When the material contains tetrahedrally coordinated (framework) aluminum, a fraction of the amine functional groups may be protonated. The doubly protonated form, in conventional notation, would be $(RNH)_2O$ and is equivalent in stoichiometry to $2 RN + H_2O$.

Any original cations can be replaced, at least in part, by calcination and/or ion exchange. Calcination will convert as-synthesised organic cations to protons. Exchange may be performed with a metal of Groups 2 through 8 of the Periodic Table or with hydrogen ions or precursors thereof such as ammonium. Catalytically active forms of ZSM-48 can result from exchange with hydrogen, rare earth metals, aluminum, and manganese.

ZSM-48 can be prepared from a reaction mixture containing a source of silica, RN, an alkali metal oxide, e.g. sodium, water, and optionally alumina, and having a composition, in terms of mole ratios of oxides, falling within the following ranges:

REACTANTS		BROAD	PREFERRED
Al_2O_3/SiO_2	=	0 to 0.02	0 to 0.01
Na/SiO_2	=	0 to 2	0.1 to 1.0
RN/SiO_2	=	0.01 to 2.0	0.05 to 1.0

$$OH^-/SiO_2 \quad = \quad 0 \text{ to } 0.25 \qquad 0 \text{ to } 0.1$$

$$H_2O/SiO_2 \quad = \quad 10 \text{ to } 100 \qquad 20 \text{ to } 70$$

$$H^+(added)/$$
$$SiO_2 \quad = \quad 0 \text{ to } 0.2 \qquad 0 \text{ to } 0.05$$

wherein RN is a C_1-C_{20} organic compound having amine functional group of $pK_a \geq 7$, and maintaining the mixture at 80-250°C until crystals of the material are formed. H^+(added) is moles acid added in excess of the moles of hydroxide added. In calculating H^+(added) and OH values, the term acid (H^+) includes both hydronium ion, whether free or coordinated, and aluminum. Thus aluminum sulfate, for example, would be considered a mixture of aluminum oxide, sulfuric acid, and water. An amine hydrochloride would be a mixture of amine and HCl.

ZSM-48 can be used as a catalyst in intimate combination with an additional component such as tungsten, vanadium, molybdenum, rhenium, nickel, cobalt, chromium, manganese, or a noble metal such as platinum or palladium where a hydrogenation-dehydrogenation function is to be performed. Such component can be introduced by exchange impregnation or physical intimate admixture, in known manner.

ZSM-48 when employed either as an adsorbent or as a catalyst should be dehydrated, at least partially, by heating to a temperature in the range of 100 to 600°C in an atmosphere, such as air, nitrogen, etc. and at atmospheric, subatmospheric or superatmospheric pressures for between 1 and 48 hours. Dehydration can also be performed at room temperature merely by placing the material in a vacuum, but a longer time is required to obtain a sufficient amount of dehydration.

Preferably, crystallization is carried out under pressure in an autoclave or static bomb reactor. Thereafter, the crystals are separated from the liquid

and recovered. The reaction mixture is prepared from
materials which supply the appropriate oxide. Such
compositions include sodium silicate, silica hydrosol,
silica gel, silicic acid, RN, sodium hydroxide, sodium
chloride, aluminum sulfate, sodium aluminate, aluminum
oxide, or aluminum itself. RN is a C_1-C_{20} organic
compound containing at least one amine functional group
of $pK_a \geq 7$ and includes such compounds as C_3-C_{18} primary,
secondary, and tertiary amines, cyclic amine, such as
piperidine, pyrrolidine and piperazine, and polyamines
such as NH_2-C_nH_{2n}-NH_2 wherein n is 4-12.

For catalytic usage ZSM-48 may be composited
with a matrix such as described in our European
Specification 0,001,695. The relative proportions of
ZSM-48 and matrix vary widely with the content of
zeolitic material ranging from about 1 to about 90
perent by weight and more usually, particularly when the
composite is prepared in the form of beads, in the range
of about 2 to about 70 percent by weight of the
composite.

Employing a catalytically active form of
ZSM-48 containing a hydrogenation component, reforming
stocks can be reformed employing a temperature between
300°C and 600°C. The pressure can be between 100 and
1000 psig but is preferably between 200 and 700 psig.
The liquid hourly space velocity is generally between
0.1 and 10, preferably between 0.5 and 4 and the
hydrogen to hydrocarbon mole ratio is generally between
1 and 20 preferably between 4 and 12.

ZSM-48 can also be used for hydroisomerization
of normal paraffins, when provided with a hydrogenation
component, e.g., platinum. Hydroisomerization is
carried out at a temperature between 100° and 400°C,
preferably 150° to 300°C, with a liquid hourly space
velocity between 0.01 and 2, preferably between 0.25 and
0.50 employing hydrogen such that the hydrogen to

hydrocarbon mole ratio is between 1:1 and 5:1.
Additionally, the catalyst can be used for olefin or
aromatic isomerization employing temperatures between
50° and 400°C.

ZSM-48 can also be used as a catalyst for
reducing the pourpoint of gas oils. This reduction is
carried out at a liquid hourly space velocity between
about 10 and about 30 and a temperature between about
400° and about 600°C. Other reactions which can be
catalysed by it, with or without a metal, e.g.,
platinum, or palladium, include
hydrogenation-dehydrogenation reactions and
desulfurization reactions, olefin polymerization
(oligomerization), aromatics alkylation with C_2-C_{12}
olefins or with C_1-C_{12} alcohols, aromatics
isomerization, disproportionation, and transalkylation
and other organic compound conversion such as the
conversion of alcohols (e.g. methanol) to hydrocarbon.

In the examples which follow ZSM-48 was
prepared from reaction mixtures of the composition
range:
(0.1 to 0.5)RN : (0.3 to 0.8)Na_2O : (0 to 0.02)Al_2O_3
SiO_2 : (20 to 70)H_2O
wherein RN is a C_1-C_{20} organic compound containing at
least one amine functional group of $pK_a \geq 7$.

Examples 1-17

A starting gel reaction mixture was prepared
from sodium silicate (27.8% SiO_2, 8.4% Na_2O, 64% H_2O), a
C_3-C_{12} diamine compound, sodium hydroxide and water.
Crystallization was carried out with stirring in a
stainless steel autoclave at 160°C. After
crystallization, the solids were separated by filtration
and then water washed followed by drying at about 100°C.
The amounts of starting material, identification of

same, product characterizations and reaction times are listed in Table 2.

The x-ray diffraction patterns of the products of Examples 5 and 7 are shown in Figures 1 and 2, respectively, and their numerical values are shown in Table 3 below. Analytical and sorption data of the products are listed in Table 4 set forth herein (Examples 18-25). Sorption was determined after dehydration at at least 200°C.

TABLE 2

Reaction Mixture Composition[a]

Ex.	Al_2O_3/SiO_2	OH/SiO_2	R	Days	Product
1	0	0	None	2	Amorphous
2	0	0	C_3DN	3	Dense phase
3	0	0	C_4DN	3	ZSM-48
4	0	0	C_5DN	2	ZSM-48
5	0	0	C_6DN	2	ZSM-48
6	0	0	C_7DN	2	ZSM-48
7	0	0	C_8DN	2	ZSM-48
8	0	0	C_9DN	2	ZSM-48
9	0	0	$C_{10}DN$	3	ZSM-48
10	0	0	$C_{12}DN$	3	b
11	0.002	0	C_8DN	3	ZSM-48
12	0.005	0	C_8DN	2	40% ZSM-48 / 60% ZSM-11
13	0.005	0	C_5DN	2	10% ZSM-11 / 90% ZSM-5
14	0	0.30	C_5DN	2	30% ZSM-5
15	0	0.15	C_5DN	2	15% ZSM-5
16	0	0.30	C_8DN	2	50% ZSM-11
17	0	0.15	C_8DN	2	ZSM-48 / 10% ZSM-11

- $H_2O/SiO_2 = 40$, $Na/SiO_2 = 0.59$, $R/SiO_2 = 0.30$.

- ZSM-48 and second unidentified component

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TABLE 3
X-RAY DIFFRACTION DATA OF ZSM-48

Product of Example 5			Product of Example 7		
2θ	D	INT	2θ	D	INT
7.45	11.87	14	7.42	11.91	15
8.65	10.22	6	8.60	10.28	7
12.26	7.22	2	12.26	7.22	3
14.46	6.13	1	14.42	6.14	2
15.06	5.88	6	15.06	5.88	6
17.45	5.08	1	17.47	5.08	1
19.05	4.66	4	19.01	4.67	4
21.13	4.20	76	21.18	4.19	84
22.74	3.91	100	22.77	3.91	100
24.74	3.60	12	24.73	3.60	13
25.70	3.47	2	25.75	3.46	2
26.10	3.41	3	26.15	3.41	3
26.36	3.38	3	26.38	3.38	4
27.60	3.23	1	27.65	3.23	1
28.83	3.10	2	28.84	3.10	3
31.32	2.86	11	31.33	2.86	13
32.83	2.73	2	32.88	2.72	2
34.05	2.63	2	34.05	2.63	2
35.44	2.53	1	35.48	2.53	1
36.30	2.47	2	36.30	2.47	3
37.66	2.39	3	37.70	2.39	3
38.40	2.34	2	38.40	2.34	2
43.18	2.10	2	43.25	2.09	3
43.77	2.07	3	43.83	2.07	4
44.58	2.03	1	44.82	2.02	1
45.12	2.01	1			
46.30	1.96	2	46.37	1.96	2
49.22	1.85	2	49.22	1.85	2
50.07	1.82	1	50.12	1.82	1
51.56	1.77	1	51.57	1.77	1

Review of the data in Table 2 shows that (1) no ZSM-48 crystallized in the absence of the diamine. (Ex. 1) (2) C_4-C_{10} diamines yielded ZSM-48 in good crystallinity (Ex. 3-9) (3) ZSM-48 can be prepared with added aluminum although with these diamines, ZSM-5 (Ex. 13) or ZSM-11 (Ex. 12) may be preferred, depending on reaction mixture composition, and (4) that an optimum OH/SiO_2 ratio exists near zero.

Example 26

This example shows that very different types of amines are effective in ZSM-48 synthesis. A reaction mixture was prepared as in Examples 1-17 except that the amine was N,N^1-bis(3-aminopropyl) piperazine. Mole ratios of reactants were as follows:

$$Al_2O_3/SiO_2 = 0$$
$$H_2O/SiO_2 = 40$$
$$OH/SiO_2 = 0$$
$$Na/SiO_2 = 0.6$$
$$R/SiO_2 = 0.3$$

after 2 days at 160°C in a stirred autoclave, ZSM-48 was obtained in good crystallinity.

Example 27

This example shows that simple amines are effective in ZSM-48 synthesis. A reaction mixture was prepared according to the procedures of Examples 1-17 except that the organic was n-hexylamine. The reaction mixture composition had the following mole ratios:

$$Al_2O_3/SiO_2 \quad = \quad < 0.01$$
$$H_2O/SiO_2 \quad = \quad 40$$
$$OH/SiO_2 \quad = \quad 0$$
$$Na/SiO_2 \quad = \quad 0.6$$
$$R/SiO_2 \quad = \quad 0.3$$

Crystallization was conducted in a stirred autoclave at 160°C for 2 days. The crystalline product was ZSM-48, contaminated with a minor portion of α-cristobalte.

Example 28

The product of Example 7 was tested for relative hexane cracking activity (α-value), and for constraint index (the ratio of the rate constant for cracking of n-hexane to that of 3-methylpentane) at 510 and at 538°C*. At 510°C, the ZSM-48 product exhibited a constraint index of 5.3 and an α of 5.0. At 538°C, the C.I. was 3.4.

* The α-test is described in a letter to the editor entitled 'Superactive Crystalline Aluminosilicate Hydrocarbon Cracking Catalysts' by P.B. Weisz and J.N. Miale, Journal of Catalysis, Vol. 4, pp. 527-529 (August 1965). The constraint index test is described in U.S. Patent 4,107,224.

TABLE 4

Characterization Data

Example	x* H_2O	SiO_2/Al_2O_3	Composition[a] Al	Na	N	DN[c]	Sorption,% (25°C)[b] NC6	CyC6
18 (Product of Example 4)	-	870	0.23	0.8	6.9	3.6	3.7	-
19 (Product of Example 5)	1.4	1320	0.15	0.7	6.2	3.3	2.5	1.7
20 (Product of Example 6)	-	1340	0.15	0.5	5.6	3.0	3.0	-
21 (Product of Example 2)	-	400	0.51	0.4	6.2	3.4	-	-
22 (Product of Example 7)	1.1 1.2	1170	0.17	0.7	5.9	3.0	3.6	2.8
23 (Product of Example 8)	-	1190	0.17	0.5	5.0	2.7	-	-
24 (Product of Example 9)	-	1290	0.17	0.5	5.2	2.7	-	-
25 (Product of Example 3)	-	910	0.17	0.3	1.4	2.6	3.3	-
						Average 3.1		

a - Per 100 SiO_2
b - Hydrocarbons, 20mm; water, 12mm
c - Diamine (per 100 SiO_2)

As previously mentioned, the X-ray diffraction pattern is preserved upon ion exchanges, possibly with minor shifts in spacing and variation in relative intensity. We have found that the calcined, sodium-exchanged form of ZSM-48 exhibits the following interplanar spacings:

TABLE 5

D(A°)	Relative Intensity
11.8 ± 0.2	W - VS
10.2 ± 0.2	W - M
7.2 ± 0.15	W - VS
4.2 ± 0.08	VS
3.9 ± 0.08	VS
3.6 ± 0.06	W
3.1 ± 0.05	W
2.85 ± 0.05	W

The relative intensities are given by the same symbols as used in Table 1 above.

The effect of calcination and sodium exchange is illustrated by Examples 29 and 30 below.

Example 29

The dried product of Example 5 (two grams) was calcined in nitrogen for 2.5 hours at 550°C followed by cooling in nitrogen for about 30 minutes. The calcined sample was ion exchanged three times with stirring at 80°C with 100 ml 2N sodium nitrate, for 2 hours each time. The sodium form sample was filtered, washed with water and dried under a heat lamp for about 30 minutes.

The X-ray diffraction data of the calcined sodium-exchange form is given below in Table 6, and the X-ray scan is shown in Figure 3 of the accompanying drawings.

TABLE

X-Ray Diffraction Data of ZSM-48

Product of Example 49

(Na-Exchanged)

2θ	D	INT
7.56	11.69	43
8.74	10.12	18
10.66	8.30	1
12.33	7.18	7
13.09	6.76	1
13.58	6.52	1
14.51	6.10	6
15.15	5.85	12
16.92	5.24	1
17.52	5.06	2
18.12	4.90	3
18.65	4.76	2
19.02	4.67	3
19.36	4.58	1
19.82	4.48	1
20.54	4.32	5
21.13	4.20	100
21.82	4.07	4
22.47	8.96	12
22.93	3.88	72
23.82	3.74	3
24.18	3.68	3
24.56	3.62	5
24.96	3.57	8
25.34	3.51	6
25.74	3.46	8
26.11	3.41	3
26.51	3.36	5
27.96	3.19	1
29.01	3.08	2
30.66	2.92	1
31.35	2.85	12
31.64	2.83	1

TABLE 6 (cont'd)

32.61	2.76	2
32.89	2.72	2
33.56	2.67	1
34.11	2.63	2
35.66	2.52	1
36.20	2.48	3
36.57	2.45	2
37.05	2.43	2
37.48	2.40	2
37.89	2.37	3
38.38	2.35	2
38.92	2.31	1
40.31	2.24	1
43.02	2.10	4
44.03	2.06	2
45.05	2.01	1
45.96	1.97	1
46.48	1.95	1
48.11	1.89	1
49.28	1.85	1
51.69	1.77	1

Example 22

The dried product of Example ? (? grams) was
calcined for 3 hours in nitrogen at 750°C followed by
cooling in ammonium gas for about 30 minutes. The
calcined sample was exchanged twice with 100 ml ?? ? ???.
nitrate solution, at ??° with stirring for about 2 hours
for each exchange. The ??? ??? sample was then
washed, dried and again calcined for 2 hours at 750°C in
nitrogen and cooled in nitrogen. This calcined sample was
ion-exchanged 3 times with stirring at ??°C in 2N sodium
nitrate solution. The ??? ? form sample was filtered,
washed with water and ??? under a heat lamp for about
30 minutes.

The X-ray diffraction data of the calcined sodium
exchanged form is given below in Table 7, and the X-ray
scan is shown in Figure ? of the accompanying drawings.

TABLE 7

X-Ray Diffraction Data of ZSM-48

Product of Example 30
(Na-Exchanged)

2θ	D	INT
7.53	11.74	48
8.71	10.15	18
10.70	8.27	1
12.30	7.20	7
13.04	6.79	1
13.62	6.50	1
14.52	6.10	8
15.10	5.87	14
16.90	5.25	1
17.53	5.06	3
18.10	4.90	3
18.64	4.76	2
19.06	4.66	2
19.62	4.52	2
20.07	4.42	2
20.47	4.34	5
21.10	4.21	100
21.93	4.05	7
22.41	3.97	12
22.91	3.88	77
23.82	3.74	4
24.16	3.68	4
24.52	3.68	6
24.90	3.58	10
25.32	3.52	7
25.72	3.46	8
26.10	3.41	4
26.50	3.36	6
29.04	3.07	2
30.71	2.91	1
31.35	2.85	12
32.55	2.75	1
32.84	2.73	2
33.56	2.67	1
34.14	2.63	2
35.64	2.52	2
36.20	2.48	3
36.59	2.46	2
37.00	2.43	2
37.40	2.40	2
37.85	2.38	4
38.34	2.35	3
38.86	2.32	1
40.33	2.24	1
43.04	2.10	4
44.06	2.06	2

CLAIMS:

1. A crystalline zeolitic material having a lattice comprising SiO_4 tetrahedra crosslinked by the sharing of oxygen atoms and characterized by the following interplanar spacings:

d(AO)	Relative Intensity
11.8 ± 0.2	M-VS
10.2 ± 0.2	M-S
7.2 ± 0.15	W
4.2 ± 0.08	VS
3.9 ± 0.08	VS
3.6 ± 0.06	W
3.1 ± 0.05	W
2.85 ± 0.05	W

2. A crystalline zeolitic material according to claim 1 the lattice of which also comprises AlO_4 tetrahedra.

3. A crystalline zeolitic material according to claim 1 or claim 2 having as the formula, in terms of mole ratios:

0-15 RN : 0-1.5 $M_{2/n}O$: 0-2 Al_2O_3 : 100 SiO_2

in which M is at least one cation of valence n and RN is an organic compound having at least one amine functional group of pk_a 7.

4. A crystalline zeolitic material according to claim 3 wherein RN is of the formula $H_2N - C_xH_{2x} - NH_2$ in which x is from 4 to 12.

5. A crystalline zeolitic material according to claim 3 wherein RN is of the formula $C_xH_{2x+1} - NH_2$ in which x is from 1 to 20.

6. A crystalline zeolitic material according to any of claims 2 to 5 which contains hydrogen, ammonium or rare earth cations.

7. A crystalline zeolitic material according to any of claims 2 to 6 in which the molar ratio of silica to alumina is from 800 to 15000.

8. A method for preparing the crystalline zeolitic material claimed in claim 1 which comprises preparing a reaction mixture containing a source of a silica, an alkali metal oxide, RN, water and alumina, and having a composition, in terms of mole ratios of oxides, falling within the following ranges:

Al_2O_3/SiO_2 = 0 to 0.02

Na/SiO_2 = 0 to 2.0

OH^-/SiO_2 = 0 to 0.25

$H^+(added)/SiO_2$ = 0 to 0.2

H_2O/SiO_2 = 10 to 100

RN/SiO_2 = 0.01 to 2.0

wherein RN is a C_1-C_{20} organic compound containing amine functional groups of pk_a 7 and maintaining said mixture at crystallization temperature until crystals are formed.

9. A method according to claim 8 wherein said reaction mixture has the composition:

Al_2O_3/SiO_2 0 to 0.01

Na/SiO_2 0.1 to 1.0

OH^-/SiO_2 0 to 0.1
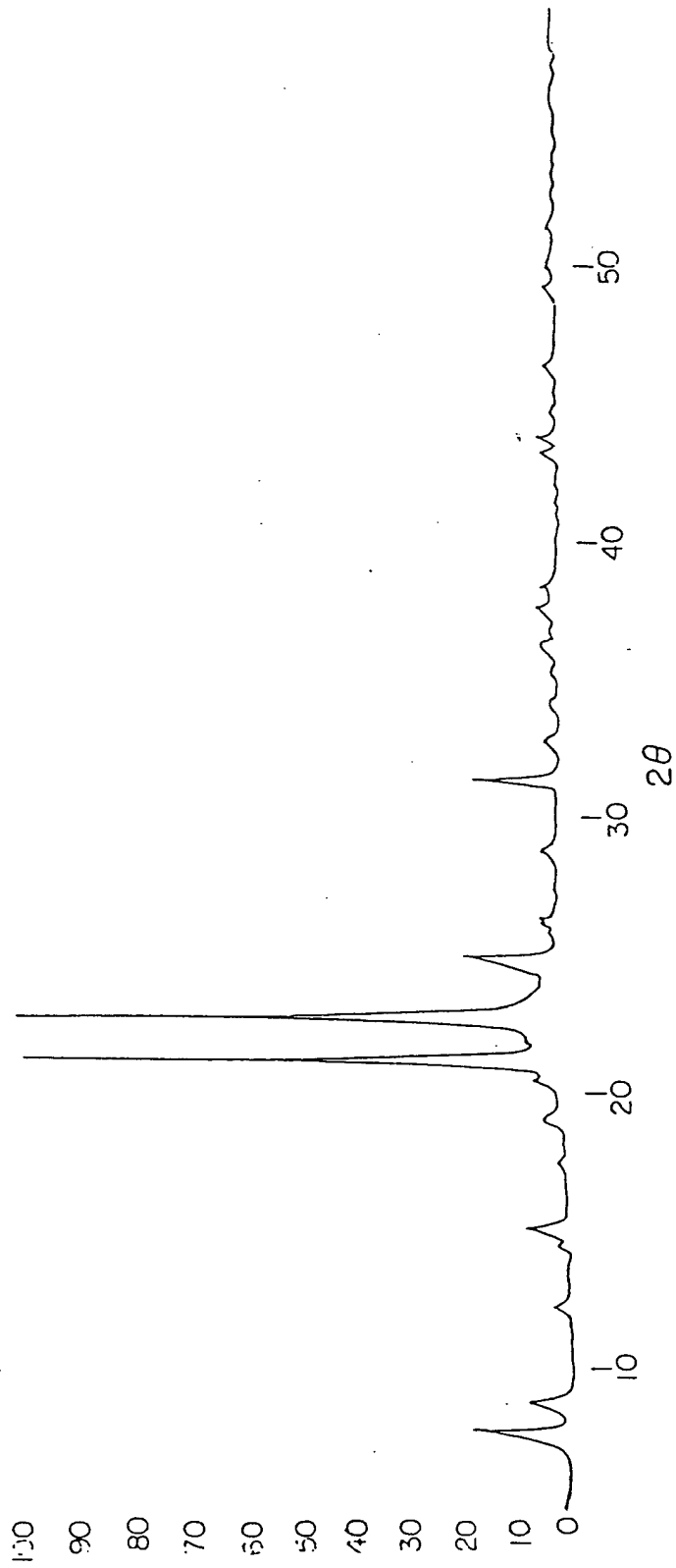
$H^+(added)/SiO_2$ 0 to 0.05

H_2O/SiO_2 20 to 70

RN/SiO_2 0.05 to 1.0

10. A method according to claim 8 or claim 9 in which RN is of the formula H_2N - C_xH_{2x} - NH_2 in which x is from 4 to 12.

11. A method according to claim 8 or claim 9 in which RN is of the formula C_xH_{2x+1} - NH_2 in which x is from 1 to 20.

12. A method according to any of claims 3 to
11 in which said temperature is in the range 80 to
250°C.

13. A process of converting an organic charge
which comprises contacting the charge under conversion
conditions with a catalyst comprising the material
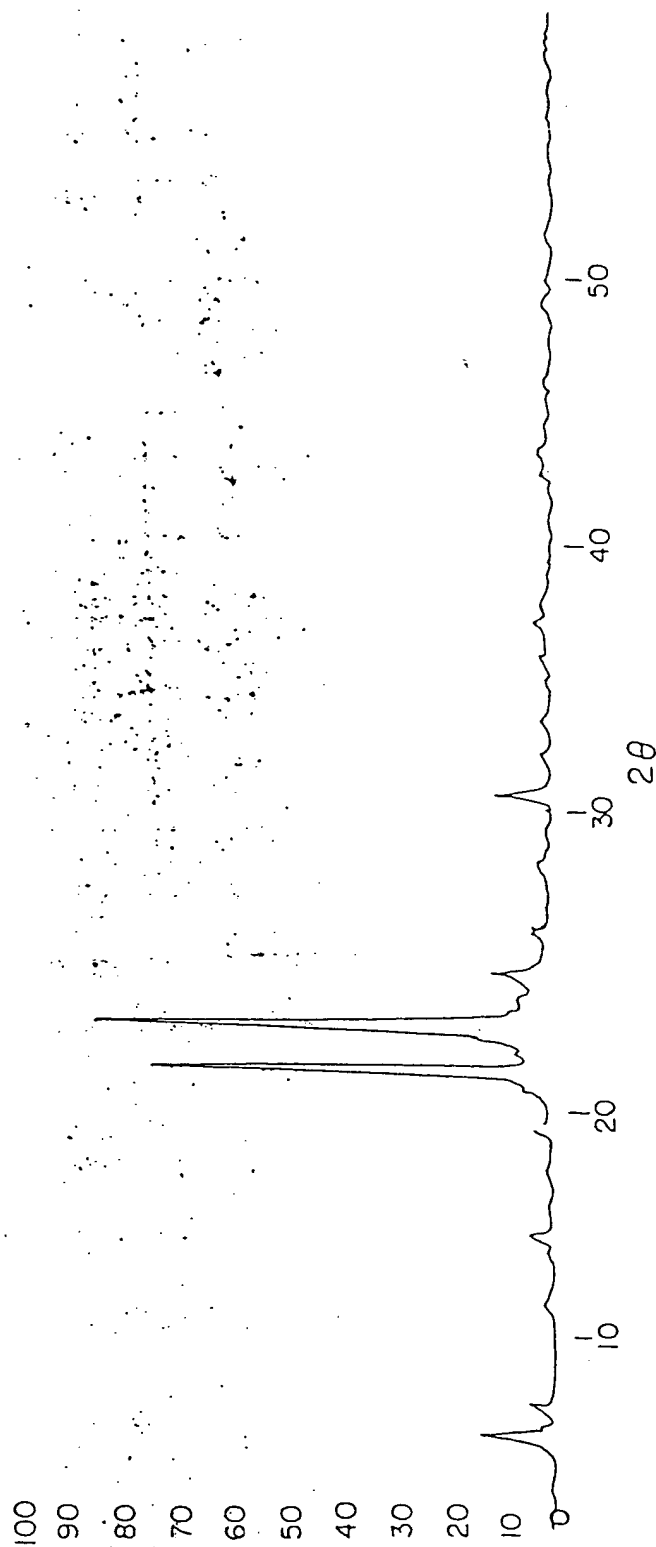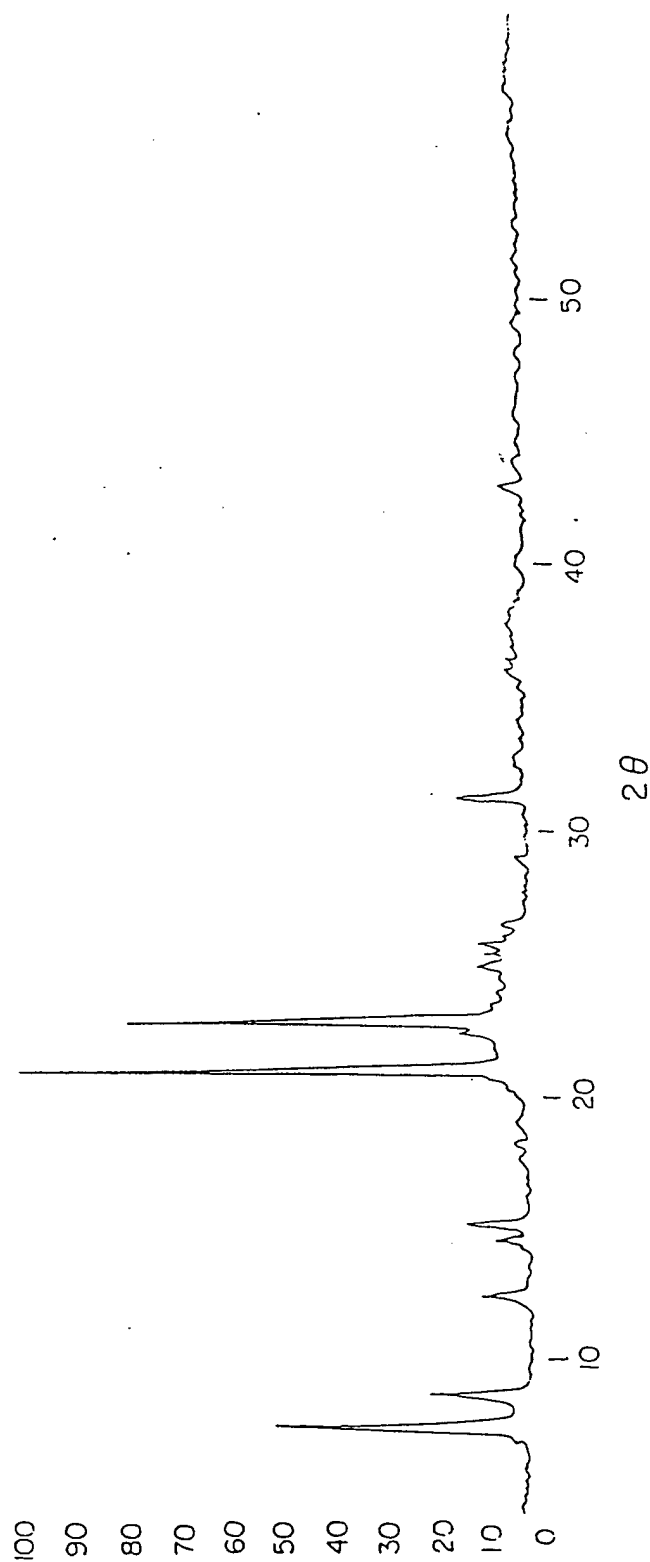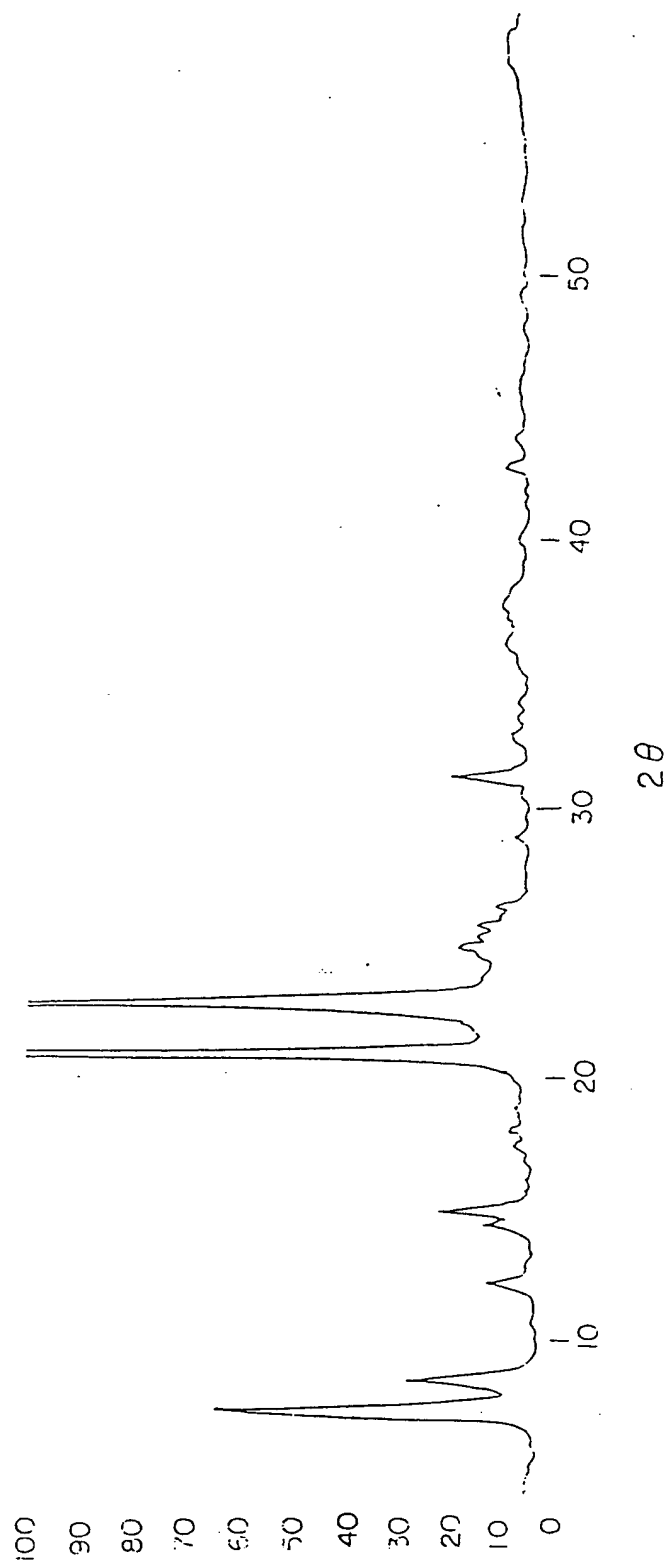claimed in any of claims 1 to 7.

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

European Patent Office

EUROPEAN SEARCH REPORT

	DOCUMENTS CONSIDERED TO BE RELEVANT		CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
D,P	EP - A1 - 0 001 695 (MOBIL OIL) --		C 01 B 33/28 B 01 J 29/28
D	US - A - 4 107 224 (MOBIL OIL) --		
A	US - A - 4 108 881 (MOBIL OIL) --		
A	US - A - 4 046 859 (MOBIL OIL) --		
A	US - A - 4 016 245 (MOBIL OIL) ----		

TECHNICAL FIELDS SEARCHED (Int.Cl.)

B 01 J 29/00
C 01 B 33/28
C 07 C 2/00
C 07 C 4/00
C 07 C 5/00
C 10 G 11/05
C 10 G 35/095

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
–: citation for other reasons

&: member of the same patent family, corresponding document

X	The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Berlin	06-05-1980	KESTEN

EPO Form 1503.1 06.78